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The Behavior of Microdisk and Microring Electrodes. Mass Transport to the Disk in the Unsteady State: *A.C. Electrochemistry*

by

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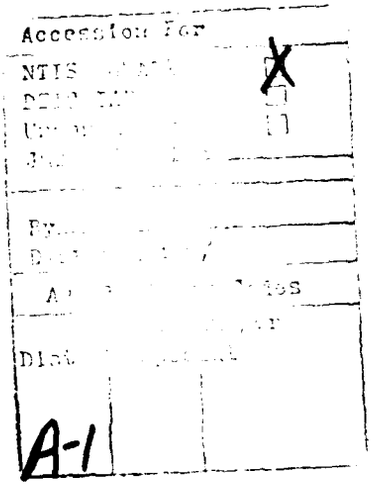

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The behaviour of microdisk and microring electrodes. Mass transport to the disk in the unsteady state

The ac response

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ABSTRACT

The analysis of the transient response of a finite geometry disk electrode (embedded in an infinite insulating plane) subjected to an AC flux perturbation is discussed. The real and imaginary components of the impedance are derived. The analysis makes use of the properties of discontinuous definite Bessel integrals.

INTRODUCTION

We have shown recently [1,2] that it is possible to derive the chronopotentiometric and chronoamperometric response of microdisk electrodes by modelling these experiments with a constant uniform flux over the microdisk and by deriving the average concentration over the surface. The properties of the discontinuous integrals of Bessel functions are used in these calculations to account for the mixed boundary conditions in the plane of the electrode (prescribed flux over the electrode surface, zero flux over the surrounding insulator surface). It is evident that the use of disontinuous integrals allows the discussion of a wide range of electrochemical techniques and in this paper we discuss the derivation of the AC impedance of a microdisk electrode for a simple redox reaction.

THEORETICAL CONSIDERATIONS

We consider the simple redox reaction

$$Ox + e^- \rightleftarrows Rd$$

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at the microdisk electrode subjected to an AC flux

$$D\,\partial c/\partial z = -Q \sin \omega t \qquad \text{say for } 0 < r < a,\ z = 0,\ t > 0 \tag{1}$$

with zero flux over the surrounding insulator surface

$$\partial c/\partial z = 0 \qquad r > a,\ z = 0,\ t > 0 \tag{2}$$

It should be noted that, as in the application of small amplitude galvanostatic or potentiostatic pulses [1,2], the uniform flux boundary condition (1) will apply rather than any boundary condition based on a uniform concentration over the surface of the microdisk. We apply conditions (1) and (2) to the solution of the differential equation governing the concentration of one of the redox species:

$$\frac{\partial c}{\partial t} = \frac{D\,\partial^2 c}{\partial r^2} + \frac{D}{r}\frac{\partial c}{\partial r} + \frac{D\,\partial^2 c}{\partial z^2} \tag{3}$$

We consider the Laplace transform of eqn. (3)

$$\frac{\partial^2 \bar{c}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{c}}{\partial r} + \frac{\partial^2 \bar{c}}{\partial z^2} - q^2 \bar{c} + \frac{c^\infty}{D} = 0 \tag{4}$$

where

$$q^2 = s/D \tag{5}$$

s is the variable of the Laplace Tranformation and c^∞ is the bulk concentration of each of the redox species. With the sustitution

$$\bar{c} = \bar{v} \exp\left[-(\alpha^2 + q^2)^{1/2} z\right] \tag{6}$$

the solution of eqn. (4) is [1]

$$\bar{c} = \frac{c^\infty}{s} + \int_0^\infty g(\alpha, q) \exp\left[-(\alpha^2 + q^2)^{1/2} z\right] J_0(\alpha r)\, d\alpha \tag{7}$$

where the function $g(\alpha,q)$ must be chosen to satisy the Laplace transforms of the boundary conditions (1) and (2):

$$\frac{\partial \bar{c}}{\partial z} = \frac{-Q\omega}{D(s^2 - \omega^2)} \qquad 0 < r < a,\ z = 0 \tag{8}$$

$$\frac{\partial \bar{c}}{\partial z} = 0 \qquad r > a,\ z = 0 \tag{9}$$

Use of the discontinuous integrals

$$\int_0^\infty J_0(\alpha r) J_1(\alpha a)\, d\alpha = \begin{cases} 0 & r > a \\ 1/2a & r = a \\ 1/a & r < a \end{cases} \tag{10}$$

shows that the alternating component of the concentration is

$$\bar{c} = \frac{q\omega a}{D(s^2 + \omega^2)} \int_0^\infty \exp\left[-(\alpha^2 + q^2)^{1/2} z\right] J_0(\alpha r) J_1(\alpha a) \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \tag{11}$$

and at $z = 0$ we have

$$\bar{c} = \frac{q\omega a}{D(s^2+\omega^2)} \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{d\alpha}{(\alpha^2+q^2)^{1/2}} \tag{12}$$

As in the analysis of the chronopotentiometric experiment, we can invert the transform before taking the integral in eqn. (12). Since we are interested only in the steady state behavior of the alternating component of the concentration, we confine attention here to the poles $s = \pm i\omega$ of the integrand of the Inversion Theorem

$$f(t) = \frac{1}{2\pi i} \int_{\lambda-i\infty}^{\lambda+i\infty} \frac{\exp(st)\, ds}{(s^2+\omega^2)(\alpha^2+s/D)^{1/2}} \tag{13}$$

The residues at these poles are

$$\frac{\exp(\pm i\omega t)}{\pm 2i\omega(\alpha^4+\omega^2/D^2)^{1/4} \exp(\pm i\theta/2)} \tag{14}$$

where

$$\tan\theta = \omega/d\alpha^2 \tag{15}$$

Thus the sum of the residues at these poles is

$$\frac{-1}{2\omega(\alpha^4+\omega^2/D^2)^{1/4}} \{i\exp[i(\omega t-\theta/2)] - i\exp[-i(\omega t-\theta/2)]\}$$

$$= \frac{1}{\omega(\alpha^4+\omega^2/D^2)^{1/4}} \sin(\omega t-\theta/2) \tag{16}$$

We apply Cauchy's Theorem to eqn. (13) (i.e. that the value of the integrand is $2\pi i$ times the sum of the residues at the poles) and use eqn. (16) in eqn. (12) to give

$$c = \frac{Qa}{D} \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{\sin(\omega t-\theta/2)\, d\alpha}{(\alpha^4+\omega^2/D^2)^{1/4}} \tag{17}$$

As in the chronopotentiometric case discussed previously, we evaluate the average concentration over the surface of the disk

$$c_{Av} = \frac{2Q}{Da} \int_0^a \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{\sin(\omega t-\theta/2) r\, dr\, d\alpha}{(\alpha^4+\omega^2/D^2)^{1/4}}$$

$$= \frac{2Q}{D^{1/2}\omega^{1/2}} \int_0^\infty [J_1(\alpha a)]^2 \frac{\sin(\omega t-\theta/2)\, d\alpha}{\alpha(1+D^2\alpha^4/\omega^2)^{1/4}} \tag{18}$$

With the substitutions

$$\beta = \alpha l \tag{19}$$

$$l^2 = D/\omega \tag{20}$$

we can write eqns. (18) and (15) as

$$c_{A_v} = \frac{2Q}{D^{1/2}\omega^{1/2}} \int_0^\infty \left[J_1\left(\frac{\beta a}{l}\right)\right]^2 \frac{\sin(\omega t - \theta/2)\, d\beta}{\beta(1+\beta^4)^{1/4}} \tag{21}$$

$$\tan\theta = 1/\beta^2 \tag{22}$$

We can use eqn. (21) in some appropriate polarization equation such as the Butler–Volmer relation

$$Q = \frac{i_0}{nF}\left\{\left(\frac{c - c_{A_v}^\infty}{c^\infty}\right)\exp\left(\frac{(1-\alpha)n\eta F}{RT}\right) - \left(\frac{C^\infty + c_{A_v}}{c^\infty}\right)\exp\left(\frac{-\alpha n\eta F}{RT}\right)\right\} \tag{23}$$

where we have assumed equal bulk concentrations of the two redox components. For sufficiently small η and c_{A_v} we linearize eqn. (23) in the usual way and expand eqn. (21) into the in-phase and quadrature components to give the real and imaginary components of the AC impedance

$$Z' = \frac{RT}{\pi nFi_0 a^2} + \frac{4RT}{\pi n^2F^2D^{1/2}\omega^{1/2}a^2c^\infty}\int_0^\infty \left[J_1\left(\beta\frac{a}{l}\right)\right]^2 \frac{\cos(\theta/2)\, d\beta}{\beta(1+\beta^4)^{1/4}}$$

$$= \frac{RT}{\pi nFi_0 a^2} + \frac{4RT}{\pi n^2F^2D^{1/2}\omega^{1/2}a^2c^\infty}\Phi_4\left(\frac{a^2\omega}{D}\right) \tag{24}$$

$$Z'' = \frac{4RT}{\pi n^2F^2D^{1/2}\omega^{1/2}a^2c^\infty}\int_0^\infty \left[J_1\left(\beta\frac{a}{l}\right)\right]^2 \frac{\sin(\theta/2)\, d\beta}{\beta(1+\beta^4)^{1/4}}$$

$$= \frac{4RT}{\pi n^2F^2D^{1/2}\omega^{1/2}a^2c^\infty}\Phi_5\left(\frac{a^2\omega}{D}\right) \tag{25}$$

The functions Φ_4 and Φ_5 are tabulated in Table 1 and Fig. 1 gives a Cole–Cole plot of the dimensionless quantities

$$\frac{\pi n^2F^2Dac^\infty}{2RT}Z' - \frac{nFDc^\infty}{2ai_0} = 2\left(\frac{D}{\omega a^2}\right)^{1/2}\Phi_4\left(\frac{a^2\omega}{D}\right) \tag{26}$$

$$\frac{\pi n^2F^2Dac^\infty}{2RT}Z'' = 2\left(\frac{D}{\omega a^2}\right)^{1/2}\Phi_5\left(\frac{a^2\omega}{D}\right) \tag{27}$$

as a function of the dimensionless frequency $a^2\omega/D$. As expected, the plot differs markedly from the plot for a large planar electrode [3]. At low frequencies, Z'' vanishes as the transport impedance becomes determined by the steady state mass transfer coefficient to the microelectrode surface. At sufficiently high frequencies the results resemble the familiar plot of the Warburg impedance and as $\omega \to \infty$ $Z'' \to 0$ and Z' is determined by the charge transfer resistance. This charge transfer resistance displaces the Cole–Cole plot along the Z' axis and R_{CT} can be obtained from both the high frequency and zero frequency limits. In contrast to measurement

TABLE 1

Values of the function $\Phi_4(a^2\omega/D)$ and $\Phi_5(a^2\omega/D)$, eqns. (24)–(27)

$a^2\omega/D$	$\Phi_4(a^2\omega/D)$	$\Phi^5(a^2\omega/D)$
0.000400	0.00841	0.000070
0.001600	0.01669	0.000276
0.003600	0.02483	0.000612
0.006400	0.03282	0.001075
0.01000	0.04068	0.001658
0.04000	0.07786	0.006213
0.09000	0.1116	0.01309
0.1600	0.1421	0.02179
0.2500	0.1695	0.03186
0.4900	0.2156	0.05465
0.6400	0.2348	0.06677
0.8100	0.2517	0.07905
1.000	0.2665	0.09131
1.210	0.2794	0.1034
1.690	0.3002	0.1266
1.960	0.3086	0.1376
2.250	0.3157	0.1480
2.890	0.3269	0.1674
3.240	0.3312	0.1762
3.610	0.3349	0.1845
4.840	0.3427	0.2064
5.760	0.3460	0.2186
6.760	0.3482	0.2292
7.840	0.3496	0.2384
9.000	0.3506	0.2464
10.24	0.3513	0.2534
11.56	0.3517	0.2595
12.96	0.3520	0.2649
14.44	0.3522	0.2696
16.00	0.3524	0.2739
25.00	0.3529	0.2899
36.00	0.3532	0.3005
64.00	0.3534	0.3138
81.00	0.3534	0.3182
100.0	0.3535	0.3217
144.0	0.3535	0.3270
196.0	0.3535	0.3308
256.0	0.3535	0.3336
324.0	0.3535	0.3359
400.0	0.3535	0.3376
506.2	0.3535	0.3394
625.0	0.3535	0.3408
756.2	0.3535	0.3420

with conventional electrodes, the fequencies are scaled by the parameter (D/a^2). As in other experiments with microelectrodes, the kinetics of fast electrode reactions become measurable by making (D/a) sufficiently large.

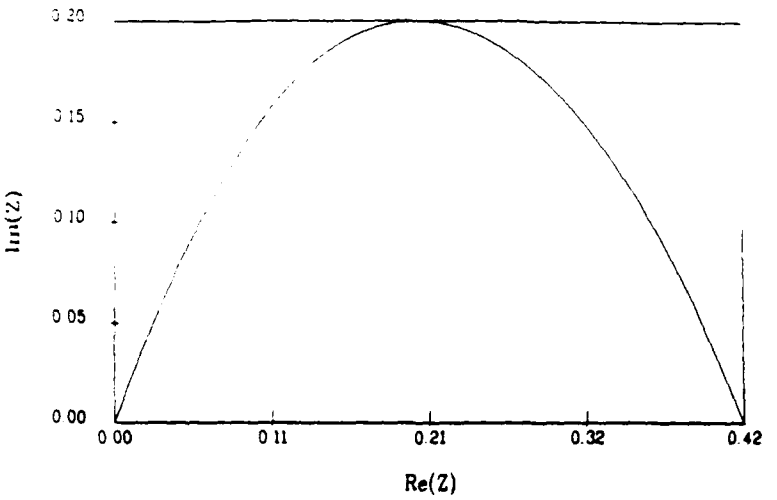

Fig. 1. Cole–Cole plot of the dimensionless impedances (24) and (25).

The equivalent circuit can be designated by Fig. 2 where M denotes the diffusional impedance of the microelectrode. It is unlikely that the uncompensated solution resistance, R_u, will have to be taken into account as the spherical potential field in the solution minimizes R_u (just as the spherical concenctration field maximizes k_m). The time constant $R_u C_{dl}$ will usually be short compared to the shortest accessible value of ω^{-1}: the response at high frequencies will in fact be similar to those of planar electrodes being determined by the product $R_{CT}C_{dl}$.

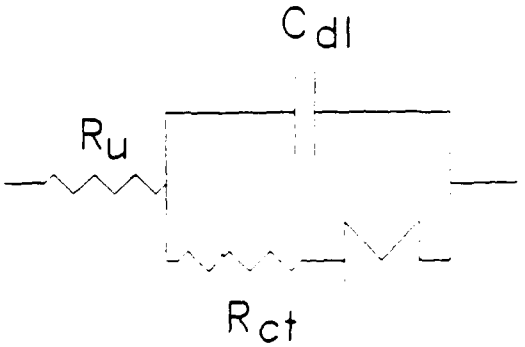

Fig. 2. Equivalent circuit for the disk microelectrode.

CONCLUSION

The simple approach to the solution of the differential equation governing mass transfer to microdisk electrodes which was used previously to discuss chronopotentiometric and chronoamperometric measurements [1,2] can evidently be used to analyze all the usual electrochemical experiments at an adequate level of approximation. Applications to reaction schemes involving coupled chemical reactions, to cyclic amperometry, and to measurements using ring electrodes will be reported elsewhere [4]. The analysis presented here opens up the use of microelectrodes in AC impedance experiments. Such measurements are likely to be particularly useful since it becomes possible to scale the frequency responses and charge transfer resistances by the parameters $(D/a)^2$ and (D/a) respectively. Therefore, as in other applications of microelectrodes to the measurement of electrochemical kinetics, the electrode dimension becomes a parameter of the experimental investigation.

ACKNOWLEDGEMENT

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GLOSSARY OF ADDITIONAL SYMBOLS USED (see also ref. 1)

C_{dl}	Double layer capacitance, μF
i	$(-1)^{1/2}$
k_m	Mass transport coefficient, cm s^{-1}
l	$(D/\omega)^{1/2}$
n	Number of electrons
R_{CT}	Uncompensated resistance, Ω
R_u	Charge transfer resistance, Ω
Z'	Real part complex impedance
Z''	Imaginary part complex impedance
θ	$\mathrm{Tan}^{-1}(\omega/D\alpha^2)$
Φ_4	$\int_0^\infty \left[J_1\left(\beta\frac{a}{l}\right)\right]^2 \frac{\cos(\theta/2)\,d\beta}{\beta(1+\beta^4)^{1/4}}$
Φ_5	$\int_0^\infty \left[J_1\left(\beta\frac{a}{l}\right)\right]^2 \frac{\sin(\theta/2)\,d\beta}{\beta(1+\beta^4)^{1/4}}$
ω	Angular frequency, Hz

not italics

REFERENCES

1 M. Fleischmann, J. Daschbach, and S. Pons, J. Electroanal. Chem., JEC 9784. 9789
2 M. Fleischmann and S. Pons, J. Electroanal. Chem., JEC 9788.
3 See for example, A. Bard and L. Faulker, Electrochemical Methods, Wiley, New York, 1980.
4 M. Fleischmann and S. Pons, J. Electroanal. Chem., JEC 9786.

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